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ON THE PERTURBATION OF THE ATOMIC STRUCTURE OF LIQUID POTASSIUM BY THE ADDITION OF KCl

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Abstract: We present and analyse the effect of the addition of up to 25% of KCl on the structure of molten potassium. At these metallic concentrations salient features of the salt structure are becoming apparent. The small angle scattering behavior and preliminary excess volume data point to strong deviation from regularity at very high metal concentration.

The solutions of the alkali metals in their molten salts have been long known [1] for their considerable change in electrical transport properties versus addition of metal. They offer an interesting example of non metal to metal transition in disordered systems. A detailed study of the concentration fluctuations near the liquid-liquid miscibility gap in the system K in KBr has already been made by small angle neutron scattering [2], [3]. On the other hand, it is quite interesting to investigate the short range order behavior of this disordered system where ionicity sets in progressively.

In the present study we have obtained the structure factors of several solutions of potassium in KCl in a concentration range where the system is metallic [4] $10^{-4} \Omega^{-1} \text{cm}^{-1} < \sigma < 10^{-3} \Omega^{-1} \text{cm}^{-1}$ and where the concentration fluctuations are definitively very small [2] (see figure 1). The experiments have been performed on the D4 machine at the Institut Laue Langevin (Grenoble) [5].

I. The experimental results - The structure factors

The structure factors of five solutions of potassium chloride in potassium from 75% to 95% in potassium content are displayed on figure 2. The smoothed structure factor of potassium given for comparison has not been extended to the whole Q range since it was found identical to the literature

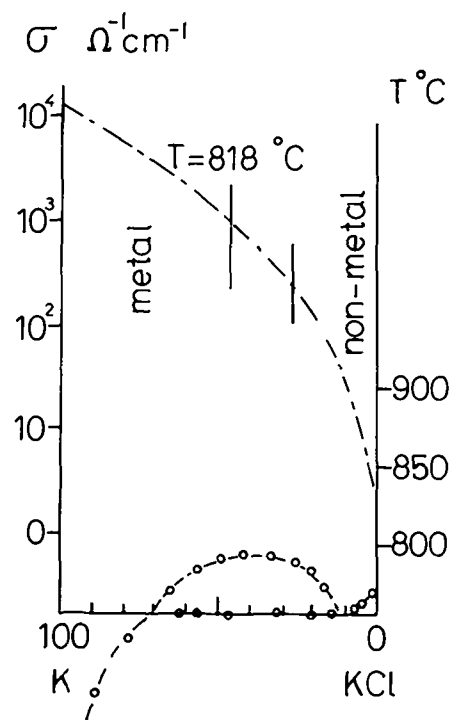


Fig. 1: Phase diagramme and electrical conductivity of K - KCl

value [6]. The data have been corrected for background, furnace, vanadium container and multiple scattering in the usual manner [7]. The incoherent scattering, assumed to be isotropic, has been obtained at large scattering angles from the ratio of incoherent to total scattering cross section. This is however still a first approach of the data ac-

quisition and treatment. As it is visible on the graph not all the runs have been performed to the same accuracy, the 90% concentration being especially poor. A close look at the low angles reveals also some difficulties left in the background correction, as noticeable on the 95% sample near 0.75 \AA^{-1} . On the other hand, detection problems have sometimes contaminated the high angle values (see the 75% sample). We believe however that the

present state of data analysis is sufficient to assert the main characteristics of those structure patterns. Several features are of interest. First, a significant small angle scattering signal is observed at all those concentrations, although it is very small at 95%. The main peak of the potassium structure factor is considerably lowered upon the addition of small amounts of KCl and has practically disappeared at a concentration of 85% in potassium. On the other hand it is at about this concentration that we begin to detect a characteristic peak of the salt structure. It is a pity that the main peak in the partial structure factor S_{CC} expressing the correlation of charges in KCl just happens to be at the main peak position of the structure factor of the pure metal preventing any analysis at this stage. However we see at the position $Q_N \approx 2.33 \text{ \AA}^{-1}$ the main peak of the partial structure factor S_{NN} , [8], expressing the correlations of density or mass in the salt. Finally, one notices also the almost structureless behavior of the 90% concentration where the disappearance of the metal peak matches the appearance of the salt peak.

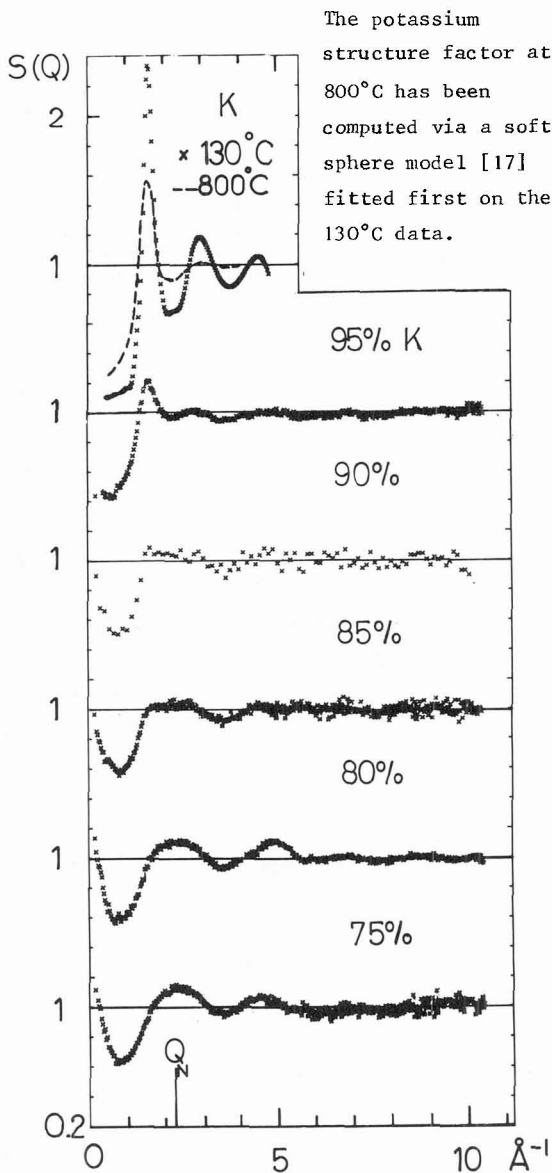


Fig. 2: The structure factors for K - KCl. Temperatures $867^\circ, 830^\circ, 800^\circ, 725^\circ, 780^\circ\text{C}$ from 75 to 95%.

II. The Small Angle Scattering

A high value of the thermodynamic limit $S(0)$ accompanied by a significant small angle scattering is not uncommon in liquid metallic alloys [9] [10]. It has been attributed to concentration fluctuations or to clustering effects. An accurate analysis of the D4 low angle data is not appropriate considering the poor experimental resolution at those angles and the difficulty to untangle the small angle signal from the foot of the structure factor main peak. It is however of interest to evaluate approximately the correlation length or the size of the corresponding fluctuations. A crude fit

of an Ornstein Zernike law on the 85% sample gives a value of about 3 Å, the same value being obtained in a Guinier analysis. Such a small fluctuation would not have been detected on conventional small angle machines such as D11 or D17 at the I.L.L. It is of course difficult to give a definite physical picture of so short fluctuations or to assess clearly if they are related to the phase separation which appears at much lower concentration in metal. Accurate thermodynamic values and more resolution in the low angle data would be quite useful. One may however make a comment on the significant feature which appear on the figure 2, i.e. the very low small angle signal at 95%.

The anomalies of the thermodynamic limit $S(o)$ in a binary system depend essentially on two terms, the value of the partial structure factor $S_{cc}(o)$ related to the derivative of the chemical potential versus concentration [11] and a contrast coefficient C which involves the difference of the neutron scattering length per unit volume between the two components [12]

$$S(o) = A + C S_{cc}(o) \quad (1)$$

the A-term depends on the isothermal compressibility of the system. The contrast is

$$C = \frac{1}{\sum_i c_i b_i^2} \left| \frac{\bar{v}_1 b_2 - \bar{v}_2 b_1}{c_1 \bar{v}_1 + c_2 \bar{v}_2} \right|^2 \quad (2)$$

where c_i , b_i and \bar{v}_i are the concentration in mole fraction, the scattering length and partial molar volume of the two constituents, K and KCl in our case (*). We have displayed on figure 3 the estimated variation of $S_{cc}(o)$ and of the contrast C versus concentration for the system K in KCl. The $S_{cc}(o)$ values have been obtained from neutron small angle scattering experiments [2] made for the system K in KBr and developed in reduced coordinates around the liquid-liquid critical point of K in KCl. On

the basis of vapour pressure measurements [13], they decrease smoothly on the potassium rich side. The contrast coefficient has been computed first on a regular solution basis (curve R) and shows a maximum near 95% in K. However, preliminary excess volume measurements as obtained from neutron transmission data display a positive excess volume in both K in KCl and K in KBr systems at concentrations rich in metal (see figure 3b). On this basis, the maximum in the contrast C would be around 85% (see curve ΔV_{EX} in figure 3). The very low small angle scattering at 95% supports therefore the idea of strong deviations from regularity in the very concentrated metallic system.

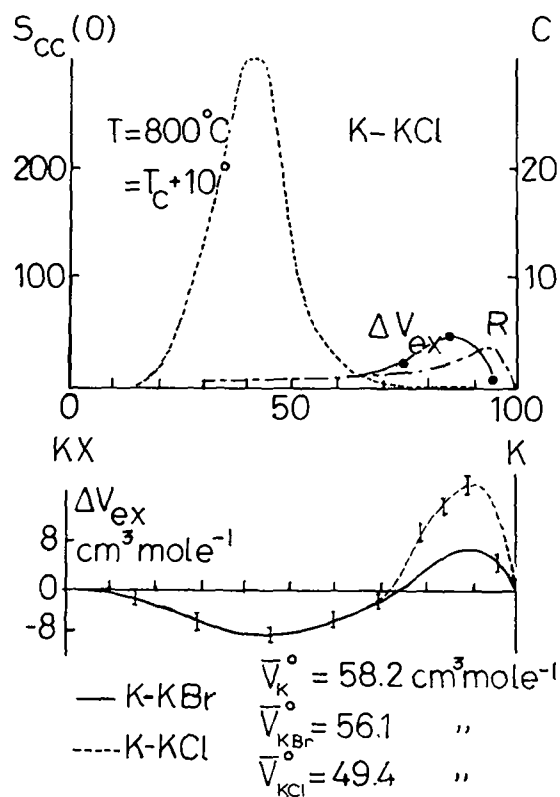


Fig. 3a) The contrast effect on $S(o)$. 3b) Excess volume and deviation from regularity.

(*) The choice of K and KCl as the two basic constituents for writing the equations (1) and (2) does not imply that these are really the two terms of the fluctuation process. Complementary experiments are required for such a determination.

III. The Fourier Transforms - Comparison with Au-Cs

The effect of addition of small quantities of KCl to potassium is well illustrated again on figure 4 by the Fourier transforms of the total structure factors. The concentrations 80% and 85% having intermediate values between those displayed have been omitted. Difficulties in Fourier transforming such as on the 90% sample which was of poor statistics have still to be overcome but the main trends are obvious. On the 90% sample and probably already on 95% appears the characteristic distance d_N of the KCl structure which is quite different from the first and second nearest neighbor d_1 and d_2 distances in potassium. We see on the total distribution function $g_N(r)$ of KCl^{nat} at 818°C [8] that the peak position d_N is typical of the first nearest neighbors i.e. the $K^+ - Cl^-$ distance. One notices however that the distance of closest

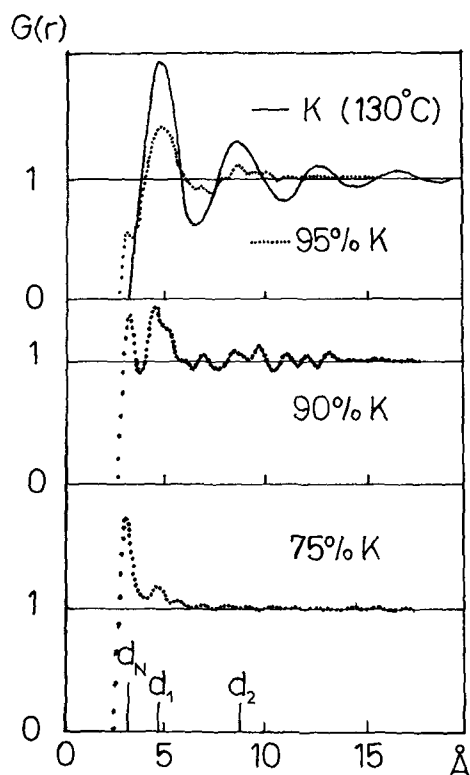


Fig. 4: The Fourier transforms of K - KCl.

approach which is nearly the same for all concentrations studied is slightly larger than for the pure salt (2.25 Å). The first neighbor metal peak considerably diminishes with the addition of KCl. At 95% the diminution is approximatively described however by simply taking into account the temperature and volume expansion effect [14].

The macroscopic properties of the M in MX and the M in MAu systems [15] present strong analogies. This is also true if one compares their structure factors [16]. In the Cs-Au case, the characteristic $Cs^+ - Au^-$ distance of the salt was observed at a concentration of 20% Au in Cs and if the analogy with K in KCl is correct, it should be detectable at even much higher concentrations of Cs.

These first results are stimulating since they point to a significant salt-like structure even at high metal concentration. It is essential however to obtain accurate values of the partial structure factors and especially the charge charge partial S_{cc} at one concentration at least, in order to throw some light on the onset of ionicity in these metallic systems.

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are 0.16 Å and 0.08 Å in the amorphous and crystalline alloys, respectively. The cause of this discrepancy is still under investigation (one possibility is a double-peak feature in the pair distribution function of the Mo-Ni distances). However, several general features can be seen from Table II. First, the distances are about 0.10 Å shorter in the amorphous than in the crystalline phase. Second, coordination number of the first shell at the Ni atoms in a-MoNi is high ~ 12 , the value found for densely close packed structure. In comparison, the crystalline phases (Tables I and II) show low coordination number ~ 7 . Third, the root mean square deviations (Debye-Waller factors) of ~ 0.10 Å in the a-MoNi are large (in comparison to the corresponding values of ~ 0.05 Å in the crystalline materials

Table 2. The distance r , Debye-Waller factor σ , and the coordination number N of the first shell of a-Mo₅₀Ni₅₀ and c-Mo₅₀Ni₅₀.

	a-Mo ₅₀ Ni ₅₀			c-Mo ₅₀ Ni ₅₀		
	$r(\text{Å})$	$\sigma(\text{Å})$	N	$r(\text{Å})$	$\sigma(\text{Å})$	N
Mo-Mo	2.76	0.09	1	2.81	0.05	2
Mo-Ni	2.43	0.10	4.7	2.57	0.04	5
Ni-Mo	2.59	0.10	3.6	2.65	0.09	1
Ni-Ni	2.36	0.09	8.4	2.47	0.11	6

Discussion

The low coordination number of $\bar{N} \sim 7$ at the first shell for both Mo and Ni edges and the appearance of the second shell at ~ 3.0 Å for the Mo edge in c-MoNi suggest that the bcc-type local short range order prevails in the c-MoNi alloy. In contrast, the absence of the second shell at 3.0 Å together with the large coordination number for the Ni edge in a-MoNi suggest that the structure of a-MoNi alloy differs from that of the crystalline alloys and may be described by a more or less dense random packing of binary spheres. This is in harmony with the results obtained by X-ray scattering measurements on many glassy metal-metal alloys, such as Zr₇₀(Pd,Ni,Co,Fe)₃₀⁽⁶⁾ and Zr-Cu and Nb-Ni⁽⁷⁾.

The Debye-Waller factor decreases with lowering temperatures but remains high of ~ 0.10 Å at 77 K for the amorphous alloys. This

indicates a substantial structural disorder in a-MoNi which is comparable to that reported for a-Pd₈₀Ge₂₀⁽⁸⁾ ($\sigma \sim 0.1$). It is premature at this point to discuss whether the unlike pair distances $r_{\text{Mo-Ni}}$ show any decrease in the amorphous state as commonly observed for many glassy alloys because factors such as large anharmonicity in σ or asymmetry in the pair distribution function can cause error in the distance determination. For the amorphous systems with large structural disorders a generalized EXAFS formulation must be used.⁽⁹⁾ The results will be published elsewhere.

The EXAFS data of Zr-Cu glassy alloys are in many features similar to those of the MoNi. Preliminary results indicate that the relative ratio of the coordination number of Zr-Zr pairs to that of Zr-Cu pairs decreases with increasing content of Cu.⁽¹⁰⁾

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